Master's Thesis of City Planning

# Application of Pyrolysis-GC/MS to Trace Lignin Phenols in Tree Leaves

## 나뭇잎 내 미량 리그닌 페놀 분석을 위한 열분해 가스 크로마토그래픽 질량분석 (Pyrolysis-GC/MS) 적용 연구

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# Application of Pyrolysis-GC/MS to Trace Lignin Phenols in Tree Leaves

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# Abstract

## Application of Pyrolysis-GC/MS to Trace Lignin Phenols in Tree Leaves

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Pyrolysis combined with gas chromatography and mass spectrometry (Py-GC/MS) is a relatively rapid method (1-3 h) for investigating polymers. Tree leaves of five conifer species and six deciduous tree species were collected from Mt. Gwanak and Mt. Baekwoon and were analyzed to check if lignin-derived phenols can be used as biomarkers to trace organic carbon sources using Py-GC/MS. Lignin is a phenylpropanoid polymer which is complex and derives essentially from the oxidation process of three p-hydroxycinnamyl alcohol monomers. These monolignols are guaiacyl (G), syringyl (S) and p-hydroxyphenyl (H) types of alcohols. Py-GC/MS detected 21 kinds of lignin-derived compounds in deciduous tree leaves whereas 17 kinds in coniferous leaves. Conifer leaves contained more G-type compounds than deciduous leaves, which were

73.7% and 65.0% of the total detected compounds, respectively. In contrast, deciduous leaves contained more S-type compounds than conifer leaves, 20.6% and 11.3%, respectively. A unique S-type lignin-derived compound, 4-methylsringol, existed in all six deciduous tree leaves, suggesting that 4-methylsringol might be used as a biomarker to trace carbon sources using Py-GC/MS. However, the leaf samples have relatively higher organic carbon concentration than soils or sediments. If the organic carbon concentration is low, samples may need to be extracted and concentrated before Py-GC/MS analysis.

**Keyword** : Pyrolysis; GC/MS; Lignin; Tree species; Conifer; Deciduous tree.
**Student Number** : 2016-24858

# Table of Contents

# Chapter 1. Introduction

Carbon (C) is one of the most indispensable element of life. Terrestrial ecosystem is a major carbon pool on earth [1], holding 650 Pg C (1 Pg = $10^{15}$g) in plants and 2300 Pg in soils [2]. In the forest ecosystem, most of the C is stored as organic materials such like litter, woods, or not totally decomposed organic residues [3].

In the terrestrial ecosystem, the largest carbon reservoir is soil organic carbon (SOC) pool [4]. The SOC sequestration in forest can be different because of the plant species, age of the stand, and climates [5-7]. SOC contents under deciduous (e.g. oak) trees can be larger than those of coniferous (e.g. pine) trees [8-10].

In South Korea, up to 40% of the forest area is composed of coniferous trees, mainly *Pinus densiflora, Larix kaempferi, Pinus rigida,* and *Pinus koraiensis* [11]. Since the coniferous trees are known to be sensitive to climate change [12], they are gradually replaced by evergreen deciduous trees [13,14]. Small alterations in the quantity or quality of leaf litter inputs could change the SOC content [15].

After cellulose, the second largest amount of natural polymer is lignin that presents in all vascular plants. Lignin is a phenylpropanoid polymer which is complex and derives essentially from the oxidation process of three p-hydroxycinnamyl alcohol monomers (Figure 1). These monolignols produce the guaiacyl (G), syringyl (S) and p-hydroxyphenyl (H) types of phenols, combining to

the lignin polymer [16–18]. The G-type contains a benzene ring with one methoxy group, S-type with two methoxy groups and H-type without methoxy group (Figure 1).

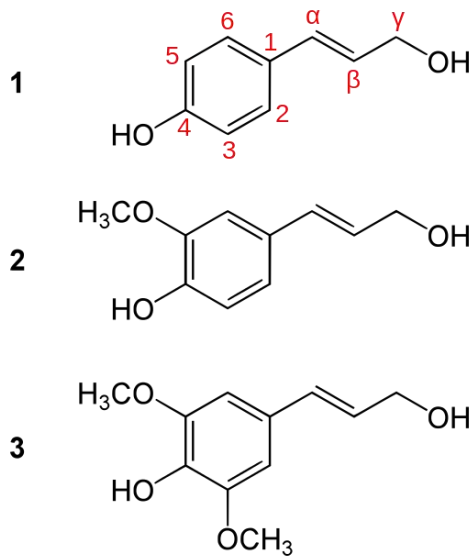



**Figure 1.** Three common monolignols: p-hydroxyphenyl (H), guaiacyl (G), and sinapyl (S) phenols.

The lignin content, inter-unit linkage distributions and monomer composition are different among species and tissues. In general, gymnosperm or coniferous lignins consist of G-types and a small amount of H-types, whereas angiosperm or deciduous lignins are consisted of G- and S-types with various S/G ratios [19,20]. Lignin phenol analysis can be used to trace the sources of SOC, which can be applied to check whether the higher SOC contents under deciduous trees than conifers are due to the effects of species.

Similar to the set of G-, S- H-type phenols, a different set of lignin phenols also has been used (Figure 2). A method using cupric

oxide (CuO) to oxidize lignin has been used [21,22]. The lignin compounds are oxidized with alkaline cupric oxide to produce six kinds of syringyl and vanillyl phenols (Figure 2). In nonwoody vascular plant tissues, lignin oxidation products also contain p-coumaric and ferulic acid [23]. In vascular plants, the CuO oxidation products, lignin-derived phenols, are particularly unique which can become indicators to distinguish tissue types and plant taxonomies.

Vanillyl phenols (V) exist in all lignin, syringyl phenols (S) are unique indicators of angiosperms, and cinnamyl phenols (C) are unique in nonwoody tissues [21]. Thus, ratios such as S/V and C/V can be used to determine the sources of lignin, i.e., angiosperms or gymnosperms, woody tissues or nonwoody tissues [21,22].

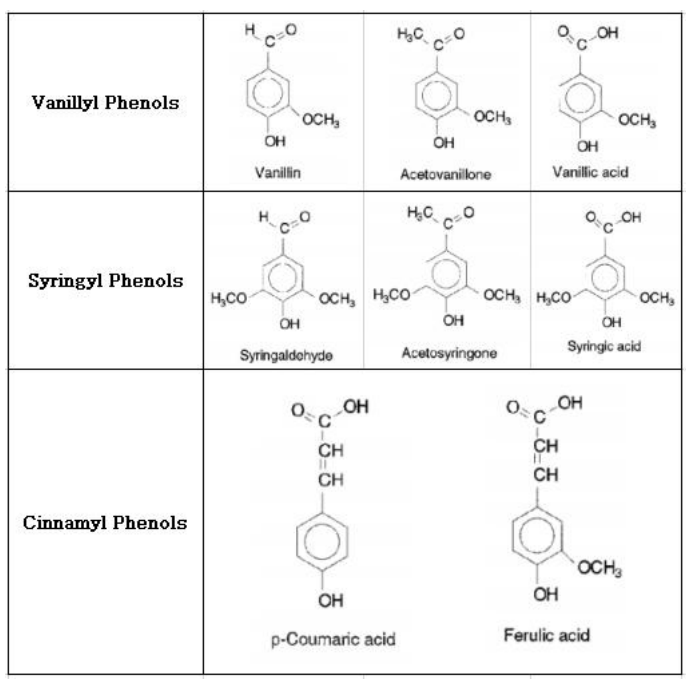



**Figure 2.** Lignin-derived phenols isolated by CuO oxidation.

Despite the advantages of the CuO oxidation, the method requires time and labor. Pyrolysis analysis with gas chromatography and mass spectrometry (Py-GC/MS) is a highly sensitive and quick method which needs relatively small amount of samples to be analyzed without any previous manipulation or isolation. Some essential advantages of Py-GC/MS are: (a) easy to prepare samples; (b) only a small amount of sample is required (less than 1 mg, usually ~100 μg); (c) the analysis lasts for a short time (20–30 min); (d) lignin polymer can be analyzed directly, not requiring pre-isolating steps, and (f) high sensitivity. The pyrolysis-GC/MS has been known as a dependable analytical method for rapidly analyzing of lignins in various wild-type plants [24-30]. The objective of this study is to investigate the lignin phenols of major conifers and broadleaf trees in South Korea using Pyrolysis-GC/MS.

# Chapter 2. Methods

## 2.1. Study Site

### 2.1.1 Mountain Gwanak (Seoul National University and Gwanak Arboretum)

Seoul National University Gwanak Campus is the main campus of Seoul National University which is located just northwest of Gwanaksan and the southern part of Seoul, South Korea. There are many tree species on campus, such as *Pinus densiflora*, *Pinus rigida*, *Taxus cuspidata*, *Ginkgo biloba*, *Zelkova serrata* and *Quercus serrata*. The Gwanak Arboretum with the area of 1,501ha is located in the southern part of Seoul, from the border of Seoul National University main campus to the Anyang valley of Gwanaksan. It is encircled by the natural forest of oak and maple at 37°25'N latitude, 126°59'E longitude, and the altitude is 90-200m. It has more than 1,100 species [31].

### 2.1.2 Mountain Baekwoon

Mountain Baekwoon is near Kwangyang City, Chollanamdo Province, South Korea. Mean annual air temperature is 14.7℃ and the mean precipitation is 1,650 mm (1946-1995). This area is a well-protected portion of the Seoul National University Forests, and a part has been designated as an ecosystem preserve by the Ministry

of Environment, Korea. Overstory vegetation consisted of natural stands of *Quercus serrata*, *Q. variabilis*, *Q.mongolica*, *Carpinus laxiflora*, *Acer pseudosieboldianum*, *A. pictum*, *Fraxinus rhynchophylla* and *F. chiisanensis*, and some planted stands of *Pinus koraiensis* and *Larix kaempferi* [32].

## 2.2. Sample Collection

Samples were collected on Mountain Gwanak (Figure 3) and Mountain Baekwoon, including five coniferous species (*Pinus densiflora, Pinus koraiensis, Pinus rigida, Taxus cuspidata and Cryptomeria japonica*) and six deciduous species (*Ginkgo biloba, Zelkova serrata, Quercus acutissima, Quercus mongolica, Quercus serrata and Acer palmatum var.*), of which *Pinus densiflora, Ginkgo biloba, Zelkova serrata, Quercus serrata* and *Acer palmatum var.* are fallen leaves, *Pinus koraiensis, Pinus rigida, Cryptomeria japonica, Quercus acutissima* and *Quercus mongolica* are air-dried fresh leaves, and *Taxus cuspidata* is oven-dried fresh leaves (Table 1). These samples were collected on July, 2018 and March, 2019 (Table 1).


**Figure 3.** Sampling sites in SNU Gwanak campus.

**Table 1. Information on tree leaves collected for py-GC analysis**

| Species | Sampling date | Site | Classification | | Sample status | | |
|---|---|---|---|---|---|---|---|
| | | | Conifers | Deciduous | Fallen | Air-dried | Oven-dried |
| *Pinus densiflora* | 2019/03/13 | Seoul National University Campus | √ | | √ | | |
| *Pinus koraiensis* | 2018/07/04 | Gwanak Arboretum | √ | | | √ | |
| *Pinus rigida* | 2018/07 | Seoul National University Campus | √ | | | √ | |
| *Taxus cuspidata* | 2019/03/13 | Seoul National University Campus | √ | | | | √ |
| *Cryptomeria japonica* | 2018/07/27, 10/09 | Mountain Baekwoon | √ | | | √ | |
| *Ginkgo biloba* | 2019/03/13 | Seoul National University Campus | | √ | √ | | |
| *Zelkova serrata* | 2019/03/13 | Seoul National University Campus | | √ | √ | | |
| *Quercus acutissima* | 2018/07/27, 10/09 | Mountain Baekwoon | | √ | | √ | |
| *Quercus mongolica* | 2018/07/04 | Gwanak Arboretum | | √ | | √ | |
| *Quercus serrata* | 2019/3/18 | Seoul National University Campus | | √ | √ | | |
| *Acer palmatum* | 2019/03/13 | Seoul National University Campus | | √ | √ | | |

## 2.3. Pyrolysis-GC/MS

The grounded dried leaf samples were weighed for 2 mg and placed in a quartz tube with 2 μl of internal standard (1.3 mg of fluoranthene/ mL acetone). The samples were pyrolyzed at 600 ℃ in an inert atmosphere (>99.9% He), the heating rate was 10 ℃/ms using the 5000 Series of CDS Pyroprobe (CDS Analytical Inc., Oxford, PA, USA) (Figure 4); the pyrolysis time was set to 20 s. The pyrolysis products were introduced into a gas chromatograph (Agilent Technologies 7890B) and a mass spectrometer detector (Agilent Technologies 5975) (Figure 4) [33].

**Figure 4.** Pyrolysis-Gas chromatography/Mass Spectrometry (Py-GC/MS).

The compound for each peak of Py-GC/MS results was identified by comparing the retention time of the peak and retention time in the data library of Seoul National University Pyeongchang Campus Biogreen Laboratory. If the retention time of the sample has a difference within ±0.2 minute with the retention time of an exact

compound in the library, it can be determined to be that compound.

The concentrations of lignin compounds in leaf samples are calculated using the equation below (eq. 1).

$$\mathrm{Rf} \times \frac{A_{target}}{A_{I.S.}} \times \frac{Q_{I.S.}}{Q_{Biomass}} = \frac{mg \rightarrow lignin}{g \rightarrow sample}(sample) \qquad \text{(eq. 1)}$$

Rf: retardation factor; $A_{target}$: area of the targeting compound: $A_{I.S.}$: area of internal standard which is Fluoranthene in this study; $Q_{I.S.}$: mass of internal standard which is 0.0026 mg in this study; $Q_{biomass}$: mass of samples is 0.002 g of each in this study.

## 2.4. Statistical Analysis

Statistical evaluation of the data has followed the method of T-testing to analyze the difference between two average values with unequal amounts of samples [34].

# Chapter 3. Results and Discussions

## 3.1. Pyrolysis-GC/MS Analysis

The products formed after a heat treatment under 600℃ are shown in Figure A1 with compound numbering.

**Table 2. Amount of different types and total lignin pyrolysis products in different kinds of tree leaves**

| Tree Species | G-type | S-type | H-type | Total |
|---|---|---|---|---|
| *Pinus Densiflora* | 11 | 1 | 4 | 16 |
| *Pinus Koraiensis* | 12 | 1 | 5 | 18 |
| *Pinus Rigida* | 9 | 1 | 3 | 13 |
| *Taxus Cuspidata* | 7 | 2 | 7 | 16 |
| *Cryptomeria Japonica* | 10 | 6 | 5 | 21 |
| Average1 | 10 | 2 | 5 | 17 |
| Variance | 3.7 | 4.7 | 2.2 | 8.7 |
| *Ginkgo Biloba* | 9 | 1 | 7 | 17 |
| *Zelkova Serrata* | 9 | 9 | 6 | 24 |
| *Quercus Acutissima* | 10 | 1 | 6 | 17 |
| *Quercus Mongolica* | 7 | 4 | 8 | 19 |
| *Quercus Serrata* | 12 | 4 | 8 | 24 |
| *Acer Palmatum Var.* | 9 | 4 | 10 | 23 |
| Average2 | 9 | 4 | 9 | 21 |
| Variance | 2.7 | 8.6 | 2.3 | 11.5 |
| P-value(A1-A2) | 0.082 | 0.023 | 0.000 | 0.002 |

Py-GC products are classified into three varieties (G-, S- and H-units) by the phenyl group structure (Table 2, Appendix Table 1-11) [35]. Average total compound number of deciduous leaves has significant difference with coniferous leaves ($p$ <0.05). Deciduous leaves have an average of 21 kinds of compounds which is more than 17 kinds in coniferous leaves. This is because deciduous trees includes not only G-type but also more types of S, while conifer leaf samples have almost G-type with less H-type and almost no S-type. In deciduous leaf samples, there are more S- and H-type (with an average of 4 and 8, respectively), which is significantly different from the number of S- and H-type in conifer leaves (with an average of 2 and 5, respectively) ($p$ <0.05). However, the number of G-type compounds Of deciduous leaves are not significantly different from that of conifer leaves ($p$ >0.05).

According to the retention time, it can be found that H- and G-type appear around 15 min to 28 min which is earlier than S-type that later than 28 min. Concentrations of G-, S- and H-type compounds in each tree species are listed in Table 3.

For all the coniferous leaves, concentration of G-type is the highest among three type compounds. The average concentration of G-, S- and H-type compounds are 15.509 mg/g, 1.009 mg/g and 2.734 mg/g, respectively. As for deciduous leaves, the average concentration of G-type compounds is 13.571 mg/g with no significant difference with coniferous leaves ($p$ <0.05). But the average concentration of S-type compounds has significantly different from coniferous leaves ($p$ <0.05) which is higher with an average of 3.038 mg/g. The S-type

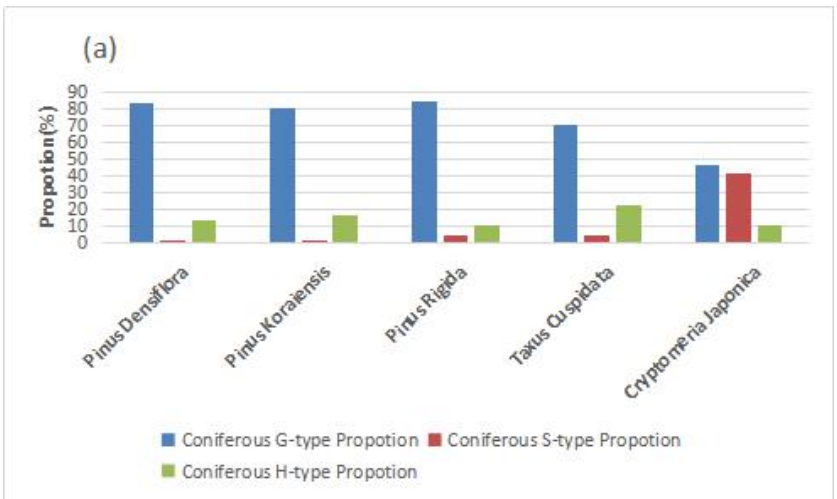
compound concentrations are particularly high in *Zelkova Serrata* and *Quercus Mongolica* such that concentrations of S-types are 8.795 mg/g and 5.707 mg/g, respectively. As for the concentration of H-type compounds, there is no statistical difference ($p$ <0.05) between deciduous leaves (with an average of 2.814 mg/g) and coniferous leave (Table 3). Above all, the concentration of S-type compounds between coniferous and deciduous leaves are significantly different ($p$ <0.05).

**Table 3. G-, S-, H-type concentrations and proportions of different tree species**

| Tree Species | Concentration (mg/g) | | |
|---|---|---|---|
| | G-type | S-type | H-type |
| *Pinus Densiflora* | 53.13 | 1.351 | 8.53 |
| *Pinus Koraiensis* | 8.59 | 0.216 | 1.782 |
| *Pinus Rigida* | 7.649 | 0.425 | 0.949 |
| *Taxus Cuspidata* | 5.22 | 0.393 | 1.694 |
| *Cryptomeria Japonica* | 2.956 | 2.66 | 0.716 |
| Average1 | 15.509 | 1.009 | 2.734 |
| Variance | 447.108 | 1.048 | 10.71 |
| *Ginkgo Biloba* | 3.182 | 0.069 | 0.923 |
| *Zelkova Serrata* | 1.59 | 8.795 | 0.345 |
| *Quercus Acutissima* | 11.847 | 0.34 | 1.54 |
| *Quercus Mongolica* | 41.879 | 5.707 | 7.202 |
| *Quercus Serrata* | 2.316 | 0.623 | 0.55 |
| *Acer Palmatum Var.* | 20.61 | 2.695 | 6.322 |
| Average2 | 13.571 | 3.038 | 2.814 |
| Variance | 246.403 | 12.462 | 9.596 |
| P-value(A1-A2) | 0.724 | 0.023 | 0.931 |

For coniferous leaves, the proportions of G-type compounds are the highest among three types, and besides *Cryptomeria japonica*, other four species all have higher proportions of H-types than S-types (Figure 5(a)). For deciduous leaves, all the samples have the highest proportions of G-type compounds except *Zelkova serrata* which with the highest proportion of S-type compounds, following with G- and H-type compounds. H-type compounds occupy more than S-type compounds in *Ginkgo biloba*, *Quercus acutissima*, *Quercus mongolica* and *Acer palmatum Var.* leaf samples, while S-type compounds occupy more than H-type compounds in *Quercus serrata* leaf sample (Figure 5(b)).

These findings are consistent with the previous studies that hardwood lignins are made up of G- and S-types with various ratios, and softwood lignins are consisted of G-types and a few H-types [36-38].



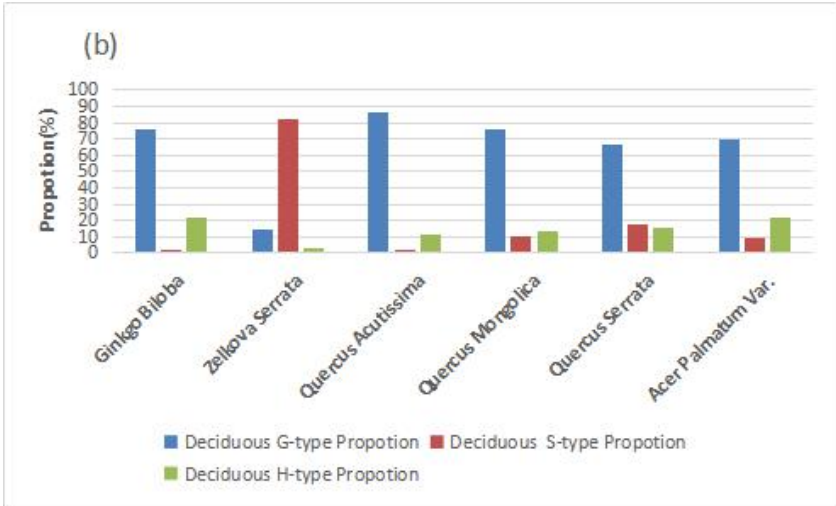



**Figure 5.** Bar graph of G-, S-, H-type compound concentration proportions. X-axis is tree species, Y-axis is proportion. Blue area is G-type proportion, red area is S-type proportion, green area is H-type proportion. (a): coniferous leaves; (b): deciduous leaves.

## 3.2 Comparison Between CuO Oxidation Products and Pyrolysis-GC/MS Compounds

While doing reviews of cupric oxide oxidation method, the oxidation products contain six vanillyl and syringyl phenols (Figure 2). As for the results of pyrolysis-GC/MS, there are some compounds that same as those in CuO oxidation method from other studies, which are vanillin, acetovanillone, syringaldehyde and acetosyringone. Lignin-derived phenols are known as particular biomarkers of vascular pants according to Hedges and Mann, 1979, which can be used to trace the organic carbon sources. vanillyl

phenols exist in all lignins, syringyl phenols are unique indicators of angiosperms, while cinnamyl phenols are special in nonwoody tissues [23]. However, the lignin-derived phenols by pyrolysis-GC/MS do not show the unique characteristic of deciduous leaves, since both coniferous and deciduous trees contain syringaldehyde and acetosyringone which belong to S, while these two S lignin-derived pheonls are unique indicators of angiosperm tissues that mentioned by previous studies. On the other hand, acetovanillone exists in all the samples, which is connected with the statement that vanillyl phenols (V) exist in all lignins, but vanillin only be found in one sample, *Quercus serrata* (Table 4).

Therefore, lignin-derived phenols maybe not be the unique indicators to divide tree species in pyrolysis-GC/MS results, some other indicators could be possible to trace the carbon sources.

**Table 4. If lignin-derived phenol Compounds are contained in Py-GC/MS results**

| Lignin Name | Type | *Pinus densiflora* | *Pinus koraiensis* | *Pinus rigida* | *Taxus cuspidata* | *Cryptomeria japonica* | *Ginkgo biloba* | *Zelkova serrata* | *Quercus acutissima* | *Quercus mongolica* | *Quercus serrata* | *Acer palmatum var.* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Vanillin** | V | | | | | | | | | | ○ | |
| **Acetovanillone** | V | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ | ○ |
| **Syringaldehyde** | S | | ○ | | ○ | ○ | | ○ | | | | |
| **Acetosyringone** | S | | | ○ | | ○ | | ○ | | | ○ | ○ |

## 3.3. Unique S-type Compound in Deciduous Leaves

After analyzing all the pyrolysis products, it has been found that there are 4 kinds of products existing in all the samples, 2 kinds of products existing in conifers only and 10 kinds of products existing in deciduous only. There is a particular phenomenon that 3,5-dimethoxy-4-hydroxytoluene also named as 4-methylsringol (Figure 6) exists in all six deciduous samples but other products do not show this unique characteristic (Table 5).

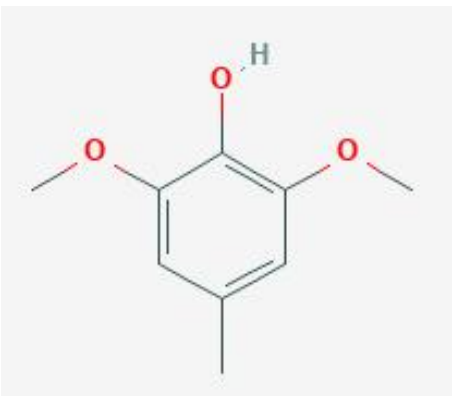



**Figure 6.** Chemical Structure of 4-methylsringol.

Not only in this study, but also other studies shows 4-methylsringol, exists in deciduous trees, such as *Populus* [39-41], *Eucalyptus globulu* [42-44], *Eucalyptus grandis* [45], *Malus domestica*, *Prununs amygdalus*, *Olea europaea* [46], *Beaucarnea recurvata*, *Quercus suber* [47], *Populus tremula x alba* [48] and *Tectona grandis* [49] (Table 6). However, in coniferous trees, 4-methylsringol does not exist [49-53]. According to these findings, it can be proved that 4-methylsringol can probably serve as a

unique compound that only exists in deciduous trees.

**Table 6. Literature review of deciduous tree with 4-methylsyringol**

| Tree Species | References |
|---|---|
| *Ginkgo biloba* | this study |
| *Zelkova serrata* | this study |
| *Quercus acutissima* | this study |
| *Quercus mongolica* | this study |
| *Quercus serrata* | this study |
| *Acer palmatum var.* | this study |
| *Populus* | Kim et al., 2014 |
| *Populus* | Meier et al., 2005 |
| *Populus* | Rencoret et al., 2016 |
| *Eucalyptus globulu* | Lourenco et al., 2013 |
| *Eucalyptus globulu* | Del rio et al., 2005 |
| *Eucalyptus globulu* | Rencoret et al., 2011 |
| *Eucalyptus grandis* | Reina et al., 2014 |
| *Malus domestica* | Sequeiros and Labidi, 2017 |
| *Prununs amygdalus* | Sequeiros and Labidi, 2017 |
| *Olea europaea* | Sequeiros and Labidi, 2017 |
| *Beaucarnea recurvata* | Sen et al., 2018 |
| *Quercus suber* | Sen et al., 2018 |
| *Populus tremula x alba* | Toraman et al., 2016 |
| *Tectona grandis* | Lourenco et al., 2015 |

**Table 5. Classifications and concentrations of lignin compounds in tree leaves**

| Classification | Compound (chemical structures showed in Appendix Table 12) | Orignin | *Pinus Densiflora* (mg/g) | *Pinus Koraiensis* (mg/g) | *Pinus Rigida* (mg/g) | *Taxus Cuspidata* (mg/g) | *Cryptomeria Japonica* (mg/g) | *Ginkgo Biloba* (mg/g) | *Zelkova Serrata* (mg/g) | *Quercus Acutissima* (mg/g) | *Quercus Mongolica* (mg/g) | *Quercus Serrata* (mg/g) | *Acer palmatum var* (mg/g). |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **All samples** | Phenol, 2-methoxy- | G | 17.698 | 1.545 | 1.498 | 1.338 | 1.267 | 0.807 | 0.630 | 3.538 | 15.707 | 0.452 | 5.080 |
| | Phenol, 2-methoxy-3-methyl- | G | 4.232 | 0.965 | 0.453 | 0.895 | 0.092 | 0.774 | 0.042 | 0.559 | 1.364 | 0.094 | 0.854 |
| | Creosol | G | 5.366 | 0.980 | 1.200 | 0.240 | 0.212 | 0.317 | 0.029 | 2.478 | 6.735 | 0.377 | 4.719 |
| | Apocynin | G | 1.295 | 0.385 | 0.138 | 0.104 | 0.182 | 0.134 | 0.029 | 0.090 | 0.491 | 0.033 | 0.240 |
| **Only Conifers** | 1,2-Benzenediol, 3-methoxy- | S ' | | | | 0.196 | 0.069 | | | | | | |
| | t-Butylhydroquinone | G ' | 0.920 | | | | | | | | | | |
| **Only Deciduous** | Phenol, 4-ethyl | H | | | | | | | | | | | 1.408 |
| | Phenol, 2,4,6-trimethyl- | H | | | | | | | | | 0.520 | 0.078 | |
| | Vanillin | G | | | | | | | | | | 0.054 | |
| | 3,5-Dimethoxy-4-hydroxytoluene | S | | | | | | 0.069 | 0.036 | 0.340 | 0.764 | 0.110 | 0.619 |
| | Butylated Hydroxytoluene | H ' | | | | | | | 0.082 | | | | |
| | Phenol, 2-methoxy-4-(2-propenyl)-, acetate | G ' | | | | | | | | | 0.277 | 0.053 | |
| | Phenol, 2-methoxy-4-(1-propenyl)-, acetate | G ' | | | | | | | 0.105 | | | | |
| | Benzenepropanol, 4-hydroxy-3-methoxy- | G | | | | | | | 0.228 | | | 0.171 | |
| | (E)-4-Propenylsyringol | S | | | | | | | 1.848 | | 1.742 | | 0.644 |
| | 4-Acetoxy-3,5-dimethoxybenzaldehyde | S ' | | | | | | | 0.781 | | | | |

# Chapter 4. Conclusions

Pyrolysis-GC/MS results show more kinds of lignin-derived compounds in deciduous leaves than coniferous leaves, the total average kinds of compound types are 21 and 17, respectively, since there are 4 kinds of S-type compounds and 8 kinds of H-type compounds in deciduous leaves, whereas only 2 kinds of S-type compounds and 5 kinds of H-type compounds in coniferous leaves. Also, the concentration of S-type compounds in deciduous leaves (with an average of 3.038 mg/g) is higher than coniferous leaves (with an average of 1.009 mg/g).

Lignin-derived phenols do not have the special characteristic, such as in CuO oxidation method, in Pyrolysis-GC results, therefore they could not be used as unique indicators to determine tree species while analyzing lignins by Pyrolysis-GC, However, a unique S-type lignin-derived compound, 4-methylsringol, existing in all six deciduous samples has been found not only in this but also some other studies showed the presenting of 4-methylsringol in their Pyrolysis-GC results of deciduous trees. According to this finding, a hypothesis has been considered that 4-methylsringol might be a unique indicator for determining tree species while analyzing lingins by Py-GC/MS method. But a challenge still presents in the analysis of soils and sediments where the concentration of organic carbon is much lower than that of leaves. If the organic carbon concentration is low, samples might need to be extracted and

concentrated before running by Py-GC/MS.

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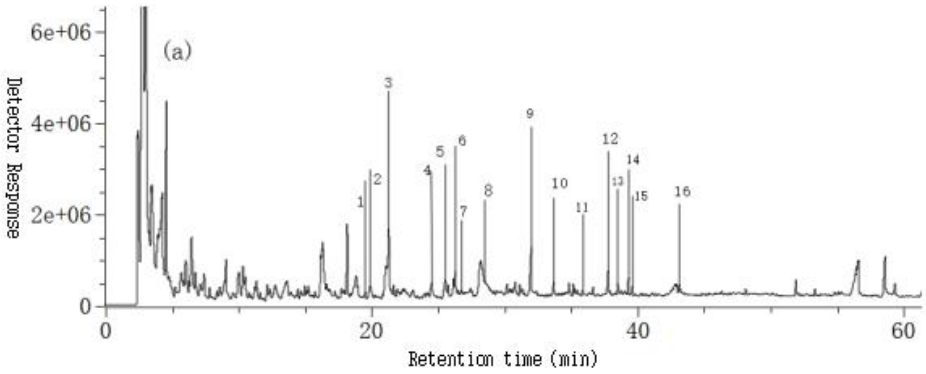
# Appendix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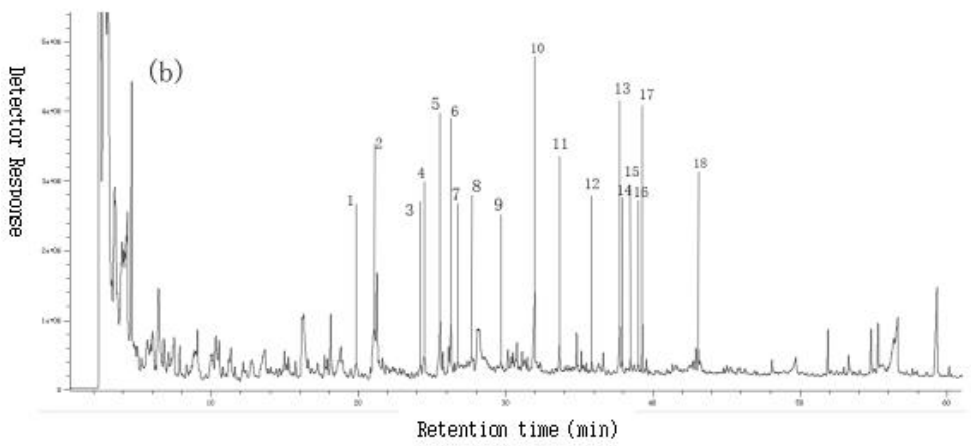
Retention time (min)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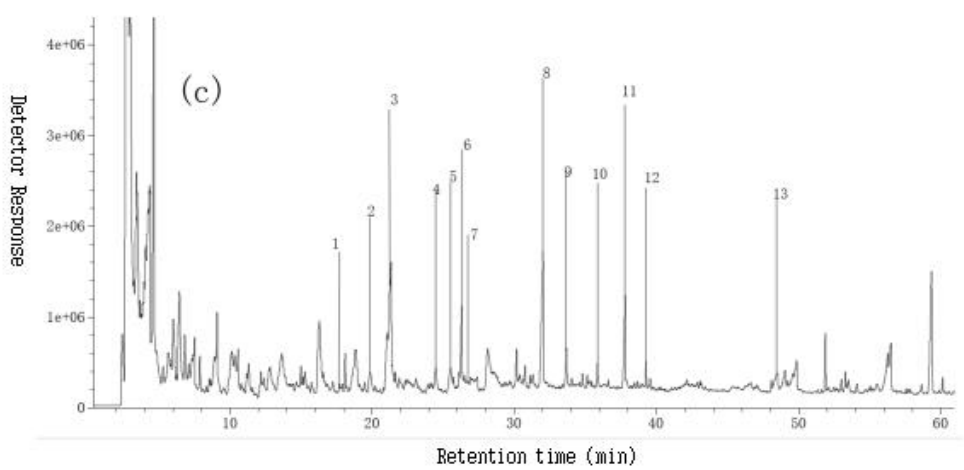
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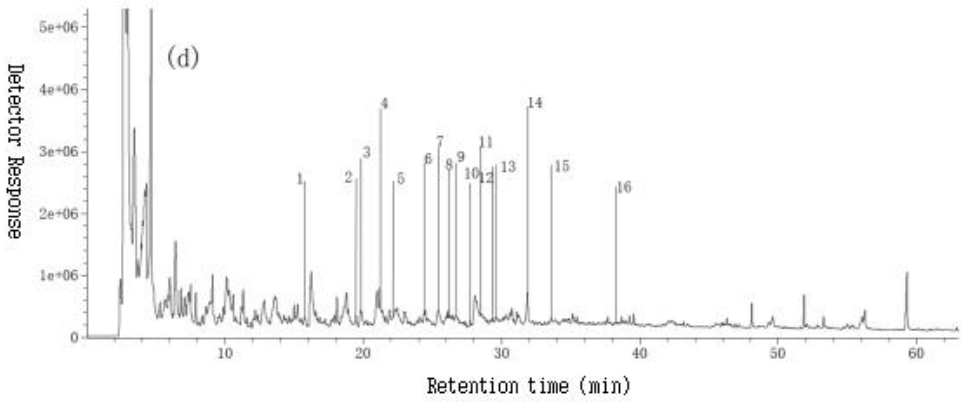
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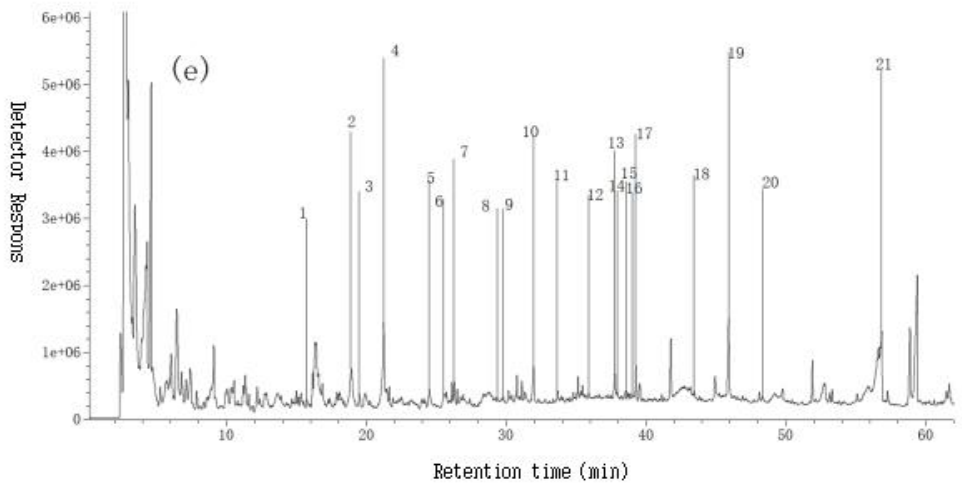
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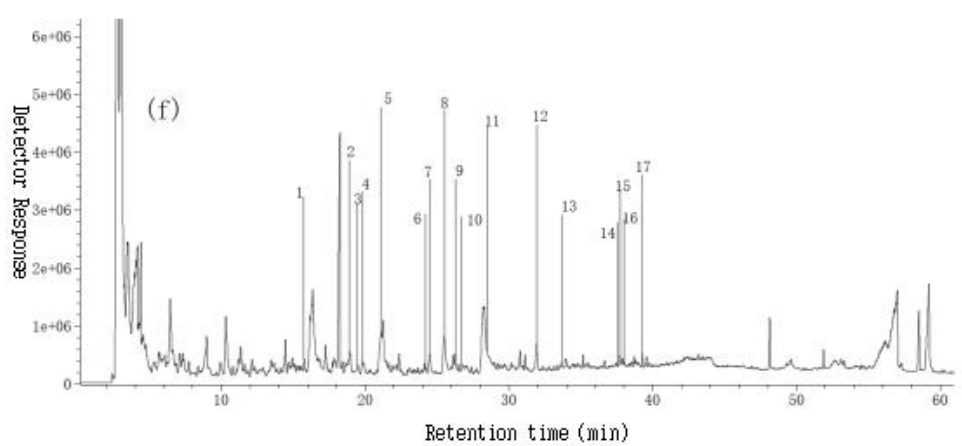
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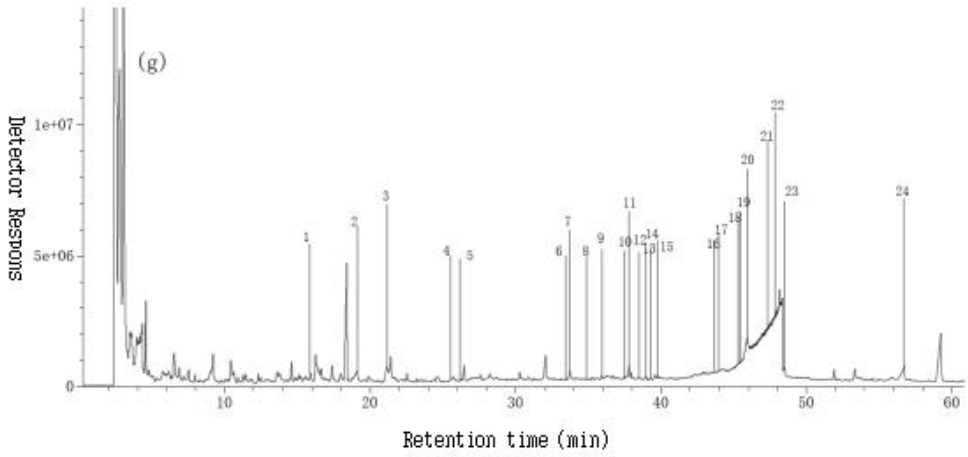
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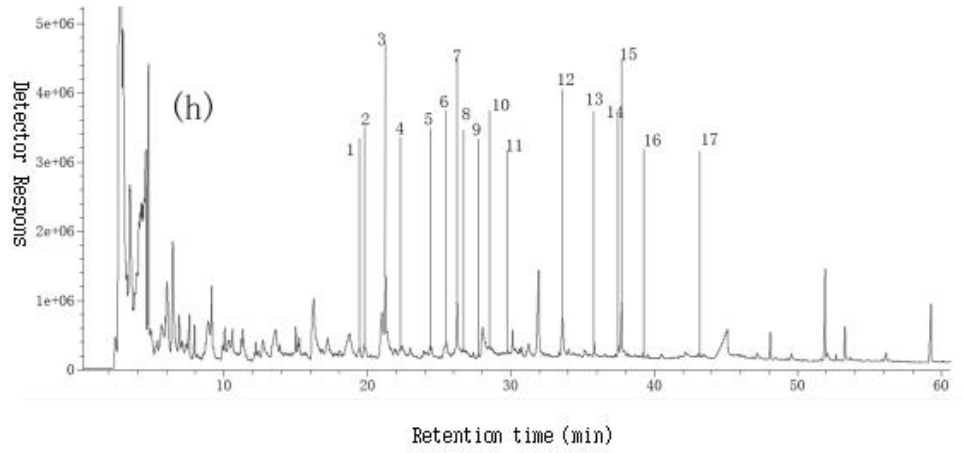
Retention time (min)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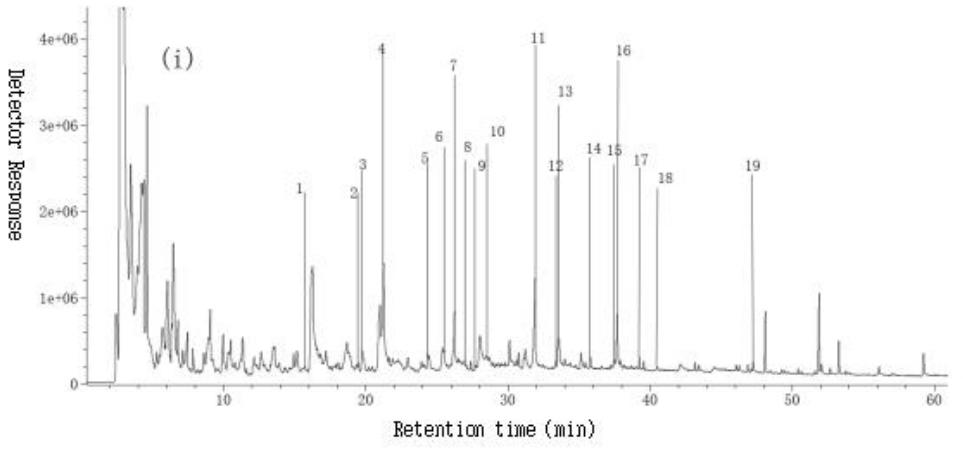
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Retention time (min)

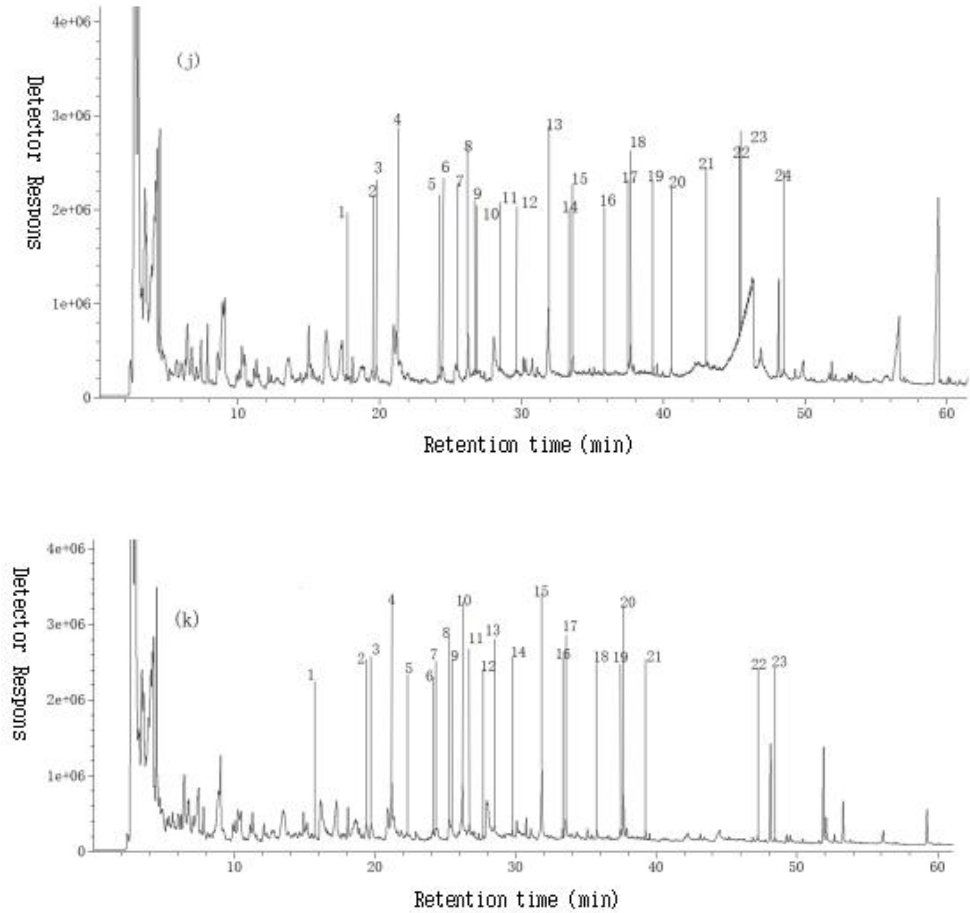



**Figure A1.** GC chromatogram of the pyrolysis products of the leaf samples (pyrolysis condition: 600℃, 20s). X-axis is the retention time, Y-axis is detector response. (a)-(k): *Pinus densiflora, Pinus koraiensis, Pinus rigida, Taxus cuspidata and Cryptomeria japonica, Ginkgo biloba, Zelkova serrata, Quercus acutissima, Quercus mongolica, Quercus serrata and Acer palmatum var.*, respectively.

**Appendix Table 1. *Pinus Densiflora* Py-GC/MS Results**

| No. | Signal: PYGC-1.D\FID1A.ch | | | | Library | | | | Concentration(mg/g) |
|---|---|---|---|---|---|---|---|---|---|
| | RT*sample* | Area | Start Time | End Time | RT*library* | Rf Value | Name | Type | |
| 1 | 19.503 | 13082582 | 19.381 | 19.654 | 19.539 | 0.59 | Phenol, 2-methyl- | H | 0.672 |
| 2 | 19.888 | 45984734 | 19.654 | 20.117 | 19.71 | 1 | Benzene, propoxy- | H ' | 4.002 |
| 3 | 21.277 | 143210947 | 21.135 | 21.408 | 21.147 | 1.42 | Phenol, 2-methoxy- | G | 17.698 |
| 4 | 24.528 | 29762320 | 24.332 | 24.708 | 24.385 | 1 | Phenol, 2,3-dimethyl- | H | 2.59 |
| 5 | 25.526 | 48625768 | 25.268 | 25.69 | 25.564 | 1 | Phenol, 2-methoxy-3-methyl- | G | 4.232 |
| 6 | 26.287 | 43422135 | 26.196 | 26.463 | 26.222 | 1.42 | Creosol | G | 5.366 |
| 7 | 26.747 | 17078964 | 26.607 | 26.89 | 26.748 | 1.17 | 1,2-Benzenediol | G ' | 1.739 |
| 8 | 28.496 | 14545971 | 28.454 | 28.549 | 28.488 | 1 | Phenol, 2-ethyl-6-methyl- | H | 1.266 |
| 9 | 32.001 | 90242483 | 31.737 | 32.215 | 31.858 | 1.65 | 2-Methoxy-4-vinylphenol | G | 12.959 |
| 10 | 33.68 | 23073914 | 33.517 | 33.823 | 33.666 | 1.77 | Eugenol | G | 3.554 |
| 11 | 35.878 | 13578560 | 35.794 | 36.19 | 35.869 | 1 | Phenol, 2-methoxy-4-(1-propenyl)- | G | 1.182 |
| 12 | 37.78 | 40272553 | 37.584 | 37.87 | 37.746 | 1 | Phenol, 2-methoxy-4-(1-propenyl)-, (Z)- | G | 3.505 |
| 13 | 38.506 | 15520709 | 38.383 | 38.637 | 38.461 | 1 | Phenol, 2,6-dimethoxy-, acetate | S ' | 1.351 |
| 14 | 39.309 | 14879614 | 39.21 | 39.4 | 39.302 | 1 | Apocynin | G | 1.295 |
| 15 | 39.596 | 10572714 | 39.4 | 39.683 | 39.423 | 1 | t-Butylhydroquinone | G ' | 0.92 |
| 16 | 43.12 | 7804650 | 43.023 | 43.172 | 43.062 | 1 | 1-Propiovanillone | G | 0.679 |
| 17 | 59.338 | 14937308 | 59.11 | 59.422 | 59.409 | 1 | Fluoranthene | I.S. | |

Rt: retention time; Rf value: retardation factor value; G: G-type; G': uncertain G-type; S: S-type; S': uncertain S-type; H: H-type; H': uncertain H-type; I.S.: internal standard.

**Appendix Table 2. *Pinus Koraiensis* Py-GC/MS Results**

| No. | Signal: PYGC-2.D\FID1A.ch | | | | Library | | | | Concentration(mg/g) |
|---|---|---|---|---|---|---|---|---|---|
| | RT*sample* | Area | Start Time | End Time | RT*library* | Rf Value | Name | Type | |
| 1 | 19.881 | 32184559 | 19.663 | 20.127 | 19.71 | 1 | Benzene, propoxy- | H ' | 0.385 |
| 2 | 21.104 | 90874598 | 20.877 | 21.173 | 21.147 | 1.42 | Phenol, 2-methoxy- | G | 1.545 |
| 3 | 24.231 | 22022900 | 24.039 | 24.335 | 24.265 | 1 | Phenol, 2,4-dimethyl- | H | 0.264 |
| 4 | 24.493 | 38428173 | 24.335 | 24.643 | 24.385 | 1 | Phenol, 2,3-dimethyl- | H | 0.46 |
| 5 | 25.574 | 80541931 | 25.225 | 25.693 | 25.564 | 1 | Phenol, 2-methoxy-3-methyl- | G | 0.965 |
| 6 | 26.306 | 57608920 | 26.191 | 26.465 | 26.222 | 1.42 | Creosol | G | 0.98 |
| 7 | 26.77 | 29769917 | 26.581 | 26.863 | 26.748 | 1.17 | 1,2-Benzenediol | G ' | 0.417 |
| 8 | 27.71 | 39769579 | 27.633 | 27.895 | 27.738 | 1 | 4-Vinylphenol | H | 0.476 |
| 9 | 29.712 | 21934538 | 29.571 | 29.779 | 29.627 | 1 | 1,2-Benzenediol, 3-methyl- | G ' | 0.263 |
| 10 | 31.999 | 105570065 | 31.73 | 32.082 | 31.858 | 1.65 | 2-Methoxy-4-vinylphenol | G | 2.086 |
| 11 | 33.68 | 34055021 | 33.527 | 33.83 | 33.666 | 1.77 | Eugenol | G | 0.722 |
| 12 | 35.875 | 19312285 | 35.726 | 36.022 | 35.869 | 1 | Phenol, 2-methoxy-4-(1-propenyl)- | G | 0.231 |
| 13 | 37.777 | 53184749 | 37.496 | 37.864 | 37.746 | 1 | Phenol, 2-methoxy-4-(1-propenyl)-, (Z)- | G | 0.637 |
| 14 | 37.936 | 15566153 | 37.864 | 38.108 | 38.084 | 1 | Homovanillyl alcohol | G | 0.186 |
| 15 | 38.491 | 18003024 | 38.396 | 38.613 | 38.461 | 1 | Phenol, 2,6-dimethoxy-, acetate | S ' | 0.216 |
| 16 | 39.046 | 16359234 | 38.852 | 39.117 | 38.965 | 1 | Benzoic acid, 4-(acetyloxy)-, methyl ester | H ' | 0.196 |
| 17 | 39.321 | 32143699 | 39.211 | 39.415 | 39.302 | 1 | Apocynin | G | 0.385 |
| 18 | 43.126 | 14421844 | 43.01 | 43.179 | 43.062 | 1 | 1-Propiovanillone | G | 0.173 |
| 19 | 59.329 | 108548015 | 59.023 | 59.556 | 59.409 | 1 | Fluoranthene | I.S. | |

**Appendix Table 3. *Pinus Rigida* Py-GC/MS Results**

| No. | Signal: PYGC-3.D\FID1A.ch | | | | Library | | | | Concentration(mg/g) |
|---|---|---|---|---|---|---|---|---|---|
| | RT*sample* | Area | Start Time | End Time | RT*library* | Rf Value | Name | Type | |
| 1 | 15.755 | 15473116 | 15.652 | 15.943 | 15.854 | 0.59 | Phenol | H | 0.107 |
| 2 | 19.884 | 37071689 | 19.663 | 20.115 | 19.71 | 1 | Benzene, propoxy- | H ' | 0.433 |
| 3 | 21.267 | 90227237 | 21.128 | 21.298 | 21.147 | 1.42 | Phenol, 2-methoxy- | G | 1.498 |
| 4 | 24.502 | 34992591 | 24.338 | 24.823 | 24.385 | 1 | Phenol, 2,3-dimethyl- | H | 0.409 |
| 5 | 25.539 | 38759487 | 25.216 | 25.686 | 25.564 | 1 | Phenol, 2-methoxy-3-methyl- | G | 0.453 |
| 6 | 26.333 | 72322439 | 26.171 | 26.434 | 26.222 | 1.42 | Creosol | G | 1.2 |
| 7 | 26.759 | 15764750 | 26.643 | 26.89 | 26.748 | 1.17 | 1,2-Benzenediol | G ' | 0.216 |
| 8 | 32.041 | 129280528 | 31.642 | 32.133 | 31.858 | 1.65 | 2-Methoxy-4-vinylphenol | G | 2.493 |
| 9 | 33.691 | 29496595 | 33.471 | 33.87 | 33.666 | 1.77 | Eugenol | G | 0.61 |
| 10 | 35.876 | 17043646 | 35.725 | 36.022 | 35.869 | 1 | Phenol, 2-methoxy-4-(1-propenyl)- | G | 0.199 |
| 11 | 37.814 | 71927199 | 37.577 | 37.889 | 37.746 | 1 | Phenol, 2-methoxy-4-(1-propenyl)-, (Z)- | G | 0.841 |
| 12 | 39.292 | 11822653 | 39.203 | 39.364 | 39.302 | 1 | Apocynin | G | 0.138 |
| 13 | 48.516 | 36325368 | 48.171 | 48.685 | 48.469 | 1 | Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- | S | 0.425 |
| 14 | 59.38 | 111216195 | 59.066 | 59.536 | 59.409 | 1 | Fluoranthene | I.S. | |

**Appendix Table 4. *Taxus Cuspidata* Py-GC/MS Results**

| No. | Signal: PYGC-4.D\FID1A.ch | | | | Library | | | | Concentration(mg/g) |
|---|---|---|---|---|---|---|---|---|---|
| | RT*sample* | Area | Start Time | End Time | RT*library* | Rf Value | Name | Type | |
| 1 | 15.768 | 15754649 | 15.651 | 15.939 | 15.854 | 0.59 | Phenol | H | 0.196 |
| 2 | 19.484 | 11935363 | 19.404 | 19.683 | 19.539 | 0.59 | Phenol, 2-methyl- | H | 0.149 |
| 3 | 19.845 | 20568767 | 19.683 | 19.894 | 19.71 | 1 | Benzene, propoxy- | H ' | 0.434 |
| 4 | 21.237 | 44634385 | 21.142 | 21.329 | 21.147 | 1.42 | Phenol, 2-methoxy- | G | 1.338 |
| 5 | 22.194 | 11972360 | 22.114 | 22.236 | 22.222 | 1 | Phenol, 2,6-dimethyl- | H | 0.253 |
| 6 | 24.424 | 13068393 | 24.321 | 24.46 | 24.385 | 1 | Phenol, 2,3-dimethyl- | H | 0.276 |
| 7 | 25.468 | 42408435 | 25.194 | 25.654 | 25.564 | 1 | Phenol, 2-methoxy-3-methyl- | G | 0.895 |
| 8 | 26.237 | 7995364 | 26.189 | 26.268 | 26.222 | 1.42 | Creosol | G | 0.24 |
| 9 | 26.742 | 28403269 | 26.574 | 26.882 | 26.748 | 1.17 | 1,2-Benzenediol | G ' | 0.701 |
| 10 | 27.755 | 4822349 | 27.615 | 27.817 | 27.738 | 1 | 4-Vinylphenol | H | 0.102 |
| 11 | 28.504 | 13512430 | 28.452 | 28.563 | 28.488 | 1 | Phenol, 2-ethyl-6-methyl- | H | 0.285 |
| 12 | 29.368 | 9290682 | 29.293 | 29.436 | 29.432 | 1 | 1,2-Benzenediol, 3-methoxy- | S ' | 0.196 |
| 13 | 29.582 | 16291625 | 29.515 | 29.743 | 29.627 | 1 | 1,2-Benzenediol, 3-methyl- | G ' | 0.344 |
| 14 | 31.893 | 45901913 | 31.627 | 32.023 | 31.858 | 1.65 | 2-Methoxy-4-vinylphenol | G | 1.598 |
| 15 | 33.62 | 10486173 | 33.455 | 33.738 | 33.54 | 0.89 | Phenol, 2,6-dimethoxy- | S | 0.197 |
| 16 | 39.279 | 4950480 | 39.163 | 39.362 | 39.302 | 1 | Apocynin | G | 0.104 |
| 17 | 59.337 | 61599832 | 59.016 | 59.53 | 59.409 | 1 | Fluoranthene | I.S. | |

Appendix Table 5. *Cryptomeria Japonica* Py-GC/MS Results

| No. | Signal: PYGC-5.D\FID1A.ch | | | | Library | | | | Concentration(mg/g) |
|---|---|---|---|---|---|---|---|---|---|
| | RT*sample* | Area | Start Time | End Time | RT*library* | Rf Value | Name | Type | |
| 1 | 15.751 | 14958143 | 15.671 | 15.944 | 15.854 | 0.59 | Phenol | H | 0.059 |
| 2 | 18.938 | 83830799 | 18.517 | 19.27 | 19.121 | 0.59 | Benzaldehyde, 2-hydroxy- | H | 0.332 |
| 3 | 19.522 | 11885426 | 19.376 | 19.704 | 19.539 | 0.59 | Phenol, 2-methyl- | H | 0.047 |
| 4 | 21.257 | 132771169 | 20.923 | 21.389 | 21.147 | 1.42 | Phenol, 2-methoxy- | G | 1.267 |
| 5 | 24.517 | 31275818 | 24.357 | 24.74 | 24.385 | 1 | Phenol, 2,3-dimethyl- | H | 0.21 |
| 6 | 25.554 | 13660764 | 25.303 | 25.59 | 25.564 | 1 | Phenol, 2-methoxy-3-methyl- | G | 0.092 |
| 7 | 26.307 | 22245471 | 26.2 | 26.438 | 26.222 | 1.42 | Creosol | G | 0.212 |
| 8 | 29.361 | 10330191 | 29.296 | 29.481 | 29.432 | 1 | 1,2-Benzenediol, 3-methoxy- | S ' | 0.069 |
| 9 | 29.813 | 9276055 | 29.764 | 29.961 | 29.821 | 1 | 3,5-Dimethoxytoluene | G ' | 0.062 |
| 10 | 31.975 | 49221526 | 31.794 | 32.196 | 31.858 | 1.65 | 2-Methoxy-4-vinylphenol | G | 0.546 |
| 11 | 33.697 | 14266382 | 33.464 | 33.847 | 33.666 | 1.77 | Eugenol | G | 0.17 |
| 12 | 35.917 | 12471795 | 35.804 | 36.005 | 35.869 | 1 | Phenol, 2-methoxy-4-(1-propenyl)- | G | 0.084 |
| 13 | 37.8 | 35374299 | 37.576 | 37.885 | 37.746 | 1 | Phenol, 2-methoxy-4-(1-propenyl)-, (Z)- | G | 0.238 |
| 14 | 37.937 | 15307243 | 37.885 | 38.156 | 38.084 | 1 | Homovanillyl alcohol | G | 0.103 |
| 15 | 38.565 | 12841979 | 38.456 | 38.649 | 38.461 | 1 | Phenol, 2,6-dimethoxy-, acetate | S ' | 0.086 |
| 16 | 39.003 | 9944418 | 38.935 | 39.135 | 38.965 | 1 | Benzoic acid, 4-(acetyloxy)-, methyl ester | H ' | 0.067 |
| 17 | 39.296 | 27085365 | 39.203 | 39.431 | 39.302 | 1 | Apocynin | G | 0.182 |
| 18 | 43.477 | 9195611 | 43.42 | 43.63 | 43.554 | 2.51 | Phenol, 2,6-dimethoxy-4-(2-propenyl)- | S | 0.155 |
| 19 | 45.941 | 88887882 | 45.749 | 46.164 | 45.94 | 2.51 | Benzaldehyde, 4-hydroxy-3,5-dimethoxy- | S | 1.5 |
| 20 | 48.362 | 8827133 | 48.236 | 48.623 | 48.469 | 1 | Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- | S | 0.059 |
| 21 | 56.893 | 117430944 | 56.71 | 57.043 | 56.886 | 1 | trans-Sinapaldehyde | S | 0.789 |
| 22 | 59.417 | 193378180 | 59.09 | 59.556 | 59.409 | 1 | Fluoranthene | I.S. | |

**Appendix Table 6. *Ginkgo Biloba* Py-GC/MS Results**

| No. | Signal: PYGC-6.D\FID1A.ch | | | | Library | | | | Concentration(mg/g) |
|---|---|---|---|---|---|---|---|---|---|
| | RT*sample* | Area | Start Time | End Time | RT*library* | Rf Value | Name | Type | |
| 1 | 15.795 | 16018163 | 15.66 | 15.872 | 15.854 | 0.59 | Phenol | H | 0.075 |
| 2 | 18.948 | 43620101 | 18.79 | 19.165 | 19.121 | 0.59 | Benzaldehyde, 2-hydroxy- | H | 0.205 |
| 3 | 19.496 | 17329212 | 19.281 | 19.688 | 19.539 | 0.59 | Phenol, 2-methyl- | H | 0.082 |
| 4 | 19.843 | 16800537 | 19.688 | 19.898 | 19.71 | 1 | Benzene, propoxy- | H ' | 0.134 |
| 5 | 21.125 | 71270197 | 20.888 | 21.173 | 21.147 | 1.42 | Phenol, 2-methoxy- | G | 0.807 |
| 6 | 24.248 | 7715032 | 24.2 | 24.353 | 24.265 | 1 | Phenol, 2,4-dimethyl- | H | 0.062 |
| 7 | 24.521 | 36060100 | 24.353 | 24.736 | 24.385 | 1 | Phenol, 2,3-dimethyl- | H | 0.288 |
| 8 | 25.531 | 97095664 | 25.298 | 25.859 | 25.564 | 1 | Phenol, 2-methoxy-3-methyl- | G | 0.774 |
| 9 | 26.281 | 27994181 | 26.202 | 26.443 | 26.222 | 1.42 | Creosol | G | 0.317 |
| 10 | 26.768 | 15791505 | 26.683 | 26.897 | 26.748 | 1.17 | 1,2-Benzenediol | G ' | 0.147 |
| 11 | 28.499 | 9804616 | 28.47 | 28.643 | 28.488 | 1 | Phenol, 2-ethyl-6-methyl- | H | 0.078 |
| 12 | 31.956 | 38466944 | 31.796 | 32.115 | 31.858 | 1.65 | 2-Methoxy-4-vinylphenol | G | 0.506 |
| 13 | 33.672 | 15482561 | 33.496 | 33.81 | 33.666 | 1.77 | Eugenol | G | 0.219 |
| 14 | 37.544 | 6934887 | 37.496 | 37.612 | 37.54 | 1.24 | 3,5-Dimethoxy-4-hydroxytoluene | S | 0.069 |
| 15 | 37.744 | 23312880 | 37.612 | 37.862 | 37.746 | 1 | Phenol, 2-methoxy-4-(1-propenyl)-, (Z)- | G | 0.186 |
| 16 | 38.052 | 11399527 | 37.993 | 38.183 | 38.084 | 1 | Homovanillyl alcohol | G | 0.091 |
| 17 | 39.301 | 16818858 | 39.227 | 39.436 | 39.302 | 1 | Apocynin | G | 0.134 |
| 18 | 59.23 | 163006148 | 58.883 | 59.523 | 59.409 | 1 | Fluoranthene | I.S. | |

Appendix Table 7. ***Zelkova Serrata*** **Py-GC/MS Results**

| No. | Signal: PYGC-7.D\FID1A.ch | | | | Library | | | | Concentration(mg/g) |
|---|---|---|---|---|---|---|---|---|---|
| | RT*sample* | Area | Start Time | End Time | RT*library* | Rf Value | Name | Type | |
| 1 | 15.934 | 24813583 | 15.795 | 16.125 | 15.854 | 0.59 | Phenol | H | 0.089 |
| 2 | 19.146 | 16747057 | 19.106 | 19.312 | 19.121 | 0.59 | Benzaldehyde, 2-hydroxy- | H | 0.06 |
| 3 | 21.168 | 72680393 | 20.949 | 21.305 | 21.147 | 1.42 | Phenol, 2-methoxy- | G | 0.63 |
| 4 | 25.577 | 6953296 | 25.435 | 25.625 | 25.564 | 1 | Phenol, 2-methoxy-3-methyl- | G | 0.042 |
| 5 | 26.209 | 3343510 | 26.085 | 26.265 | 26.222 | 1.42 | Creosol | G | 0.029 |
| 6 | 33.483 | 3494713 | 33.355 | 33.547 | 33.363 | 1 | Phenol, 4-(2-propenyl)- | H | 0.021 |
| 7 | 33.766 | 26147591 | 33.547 | 33.919 | 33.666 | 1.77 | Eugenol | G | 0.282 |
| 8 | 34.908 | 5120549 | 34.779 | 35.05 | 34.97 | 1 | Benzaldehyde, 4-hydroxy- | H | 0.031 |
| 9 | 35.945 | 6010305 | 35.805 | 36.005 | 35.869 | 1 | Phenol, 2-methoxy-4-(1-propenyl)- | G | 0.037 |
| 10 | 37.484 | 4706992 | 37.416 | 37.541 | 37.54 | 1.24 | 3,5-Dimethoxy-4-hydroxytoluene | S | 0.036 |
| 11 | 37.828 | 34144977 | 37.697 | 37.902 | 37.746 | 1 | Phenol, 2-methoxy-4-(1-propenyl)-, (Z)- | G | 0.208 |
| 12 | 38.482 | 6794858 | 38.372 | 38.57 | 38.461 | 1 | Phenol, 2,6-dimethoxy-, acetate | S ' | 0.041 |
| 13 | 38.973 | 9985563 | 38.857 | 39.123 | 38.965 | 1 | Benzoic acid, 4-(acetyloxy)-, methyl ester | H ' | 0.061 |
| 14 | 39.313 | 4720729 | 39.24 | 39.428 | 39.302 | 1 | Apocynin | G | 0.029 |
| 15 | 39.821 | 13430615 | 39.718 | 39.913 | 39.852 | 1 | Butylated Hydroxytoluene | H ' | 0.082 |
| 16 | 43.586 | 13525932 | 43.528 | 43.619 | 43.554 | 2.51 | Phenol, 2,6-dimethoxy-4-(2-propenyl)- | S | 0.207 |
| 17 | 43.977 | 17246482 | 43.922 | 44.016 | 43.989 | 1 | Phenol, 2-methoxy-4-(1-propenyl)-, acetate | G ' | 0.105 |
| 18 | 45.369 | 37822450 | 45.307 | 45.414 | 45.413 | 2.51 | (Z)-4-Propenylsyringol | S | 0.579 |
| 19 | 45.472 | 37364138 | 45.414 | 45.511 | 45.511 | 1 | Benzenepropanol, 4-hydroxy-3-methoxy- | G | 0.228 |
| 20 | 45.957 | 300914215 | 45.703 | 46.114 | 45.94 | 2.51 | Benzaldehyde, 4-hydroxy-3,5-dimethoxy- | S | 4.607 |
| 21 | 47.359 | 120714099 | 47.301 | 47.406 | 47.388 | 2.51 | (E)-4-Propenylsyringol | S | 1.848 |
| 22 | 47.866 | 128102214 | 47.808 | 47.898 | 47.891 | 1 | 4-Acetoxy-3,5-dimethoxybenzaldehyde | S ' | 0.781 |
| 23 | 48.525 | 33892867 | 48.417 | 48.617 | 48.469 | 1 | Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- | S | 0.207 |
| 24 | 56.752 | 79995362 | 56.256 | 56.887 | 56.886 | 1 | trans-Sinapaldehyde | S | 0.488 |
| 25 | 59.253 | 213119357 | 58.83 | 59.43 | 59.409 | 1 | Fluoranthene | I.S. | |

**Appendix Table 8.** ***Quercus Acutissima*** **Py-GC/MS Results**

| No. | Signal: PYGC-8.D\FID1A.ch | | | | Library | | | | Concentration(mg/g) |
|---|---|---|---|---|---|---|---|---|---|
| | RT*sample* | Area | Start Time | End Time | RT*library* | Rf Value | Name | Type | |
| 1 | 19.458 | 15279270 | 19.225 | 19.672 | 19.539 | 0.59 | Phenol, 2-methyl- | H | 0.244 |
| 2 | 19.809 | 14116395 | 19.672 | 19.87 | 19.71 | 1 | Benzene, propoxy- | H ' | 0.382 |
| 3 | 21.292 | 92139594 | 21.14 | 21.357 | 21.147 | 1.42 | Phenol, 2-methoxy- | G | 3.538 |
| 4 | 22.323 | 5811934 | 22.098 | 22.363 | 22.222 | 1 | Phenol, 2,6-dimethyl- | H | 0.157 |
| 5 | 24.391 | 8164051 | 24.312 | 24.439 | 24.385 | 1 | Phenol, 2,3-dimethyl- | H | 0.221 |
| 6 | 25.523 | 20664525 | 25.451 | 25.659 | 25.564 | 1 | Phenol, 2-methoxy-3-methyl- | G | 0.559 |
| 7 | 26.281 | 64535870 | 26.038 | 26.419 | 26.222 | 1.42 | Creosol | G | 2.478 |
| 8 | 26.74 | 7027749 | 26.69 | 26.796 | 26.748 | 1.17 | 1,2-Benzenediol | G ' | 0.222 |
| 9 | 27.752 | 3544980 | 27.643 | 27.821 | 27.738 | 1 | 4-Vinylphenol | H | 0.096 |
| 10 | 28.535 | 16305245 | 28.482 | 28.663 | 28.488 | 1 | Phenol, 2-ethyl-6-methyl- | H | 0.441 |
| 11 | 29.783 | 9057431 | 29.717 | 29.903 | 29.821 | 1 | 3,5-Dimethoxytoluene | G ' | 0.245 |
| 12 | 33.622 | 58896671 | 33.436 | 33.892 | 33.666 | 1.77 | Eugenol | G | 2.819 |
| 13 | 35.838 | 14120286 | 35.711 | 35.999 | 35.869 | 1 | Phenol, 2-methoxy-4-(1-propenyl)- | G | 0.382 |
| 14 | 37.511 | 10147846 | 37.356 | 37.586 | 37.54 | 1.24 | 3,5-Dimethoxy-4-hydroxytoluene | S | 0.34 |
| 15 | 37.752 | 52771879 | 37.586 | 37.894 | 37.746 | 1 | Phenol, 2-methoxy-4-(1-propenyl)-, (Z)- | G | 1.427 |
| 16 | 39.264 | 3327308 | 39.19 | 39.374 | 39.302 | 1 | Apocynin | G | 0.09 |
| 17 | 43.177 | 3264384 | 43.1 | 43.299 | 43.062 | 1 | 1-Propiovanillone | G | 0.088 |
| 18 | 59.308 | 48079524 | 58.963 | 59.477 | 59.409 | 1 | Fluoranthene | I.S. | |

Appendix **Table 9.** ***Quercus Mongolica*** **Py-GC/MS Results**

| No. | Signal: PYGC-9.D\FID1A.ch | | | | Library | | | | Concentration(mg/g) |
|---|---|---|---|---|---|---|---|---|---|
| | RT*sample* | Area | Start Time | End Time | RT*library* | Rf Value | Name | Type | |
| 1 | 15.725 | 6830021 | 15.598 | 15.863 | 15.854 | 0.59 | Phenol | H | 0.368 |
| 2 | 19.48 | 6048117 | 19.423 | 19.617 | 19.539 | 0.59 | Phenol, 2-methyl- | H | 0.326 |
| 3 | 19.761 | 28804131 | 19.617 | 20.043 | 19.71 | 1 | Benzene, propoxy- | H ' | 2.628 |
| 4 | 21.257 | 121237294 | 21.105 | 21.579 | 21.147 | 1.42 | Phenol, 2-methoxy- | G | 15.707 |
| 5 | 24.371 | 9679491 | 24.281 | 24.422 | 24.385 | 1 | Phenol, 2,3-dimethyl- | H | 0.883 |
| 6 | 25.506 | 14952327 | 25.474 | 25.684 | 25.564 | 1 | Phenol, 2-methoxy-3-methyl- | G | 1.364 |
| 7 | 26.251 | 51982106 | 26.052 | 26.418 | 26.222 | 1.42 | Creosol | G | 6.735 |
| 8 | 26.966 | 5697608 | 26.817 | 27.037 | 26.983 | 1 | Phenol, 2,4,6-trimethyl- | H | 0.52 |
| 9 | 27.723 | 3385957 | 27.64 | 27.793 | 27.738 | 1 | 4-Vinylphenol | H | 0.309 |
| 10 | 28.527 | 19446852 | 28.383 | 28.607 | 28.488 | 1 | Phenol, 2-ethyl-6-methyl- | H | 1.774 |
| 11 | 31.928 | 83659331 | 31.596 | 32.123 | 31.858 | 1.65 | 2-Methoxy-4-vinylphenol | G | 12.594 |
| 12 | 33.375 | 4322556 | 33.252 | 33.429 | 33.363 | 1 | Phenol, 4-(2-propenyl)- | H | 0.394 |
| 13 | 33.59 | 39425553 | 33.429 | 33.76 | 33.54 | 0.89 | Phenol, 2,6-dimethoxy- | S | 3.201 |
| 14 | 35.816 | 7565992 | 35.694 | 36.003 | 35.869 | 1 | Phenol, 2-methoxy-4-(1-propenyl)- | G | 0.69 |
| 15 | 37.475 | 6750596 | 37.394 | 37.546 | 37.54 | 1.24 | 3,5-Dimethoxy-4-hydroxytoluene | S | 0.764 |
| 16 | 37.709 | 44048549 | 37.546 | 37.87 | 37.746 | 1 | Phenol, 2-methoxy-4-(1-propenyl)-, (Z)- | G | 4.019 |
| 17 | 39.267 | 5386872 | 39.139 | 39.343 | 39.302 | 1 | Apocynin | G | 0.491 |
| 18 | 40.508 | 3037799 | 40.357 | 40.663 | 40.418 | 1 | Phenol, 2-methoxy-4-(2-propenyl)-, acetate | G ' | 0.277 |
| 19 | 47.27 | 7604720 | 47.18 | 47.463 | 47.388 | 2.51 | (E)-4-Propenylsyringol | S | 1.742 |
| 20 | 59.267 | 14248260 | 59.05 | 59.537 | 59.409 | 1 | Fluoranthene | I.S. | |

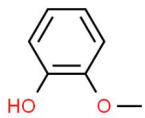
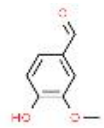
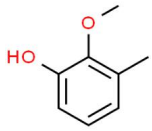
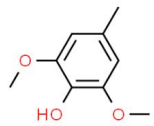
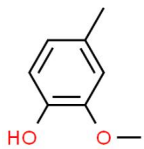
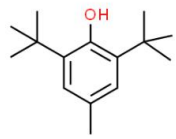
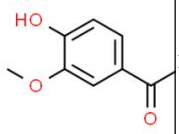
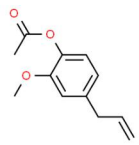
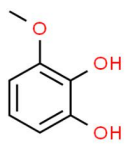
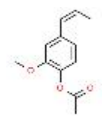
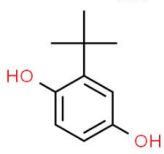
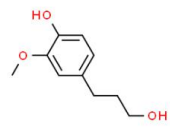
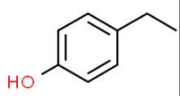
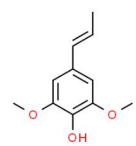
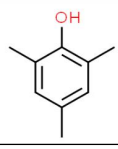
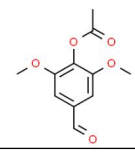
**Appendix Table 10. *Quercus Serrata* Py-GC/MS Results**

| No. | Signal: PYGC-10.D\FID1A.ch | | | | Library | | | | Concentration(mg/g) |
|---|---|---|---|---|---|---|---|---|---|
| | RT*sample* | Area | Start Time | End Time | RT*library* | Rf Value | Name | Type | |
| 1 | 15.757 | 15529322 | 15.635 | 15.996 | 15.854 | 0.59 | Phenol | H | 0.059 |
| 2 | 19.488 | 22394210 | 19.262 | 19.643 | 19.539 | 0.59 | Phenol, 2-methyl- | H | 0.085 |
| 3 | 19.777 | 19454680 | 19.643 | 19.918 | 19.71 | 1 | Benzene, propoxy- | H ' | 0.126 |
| 4 | 21.231 | 49303615 | 21.131 | 21.34 | 21.147 | 1.42 | Phenol, 2-methoxy- | G | 0.452 |
| 5 | 24.198 | 6396255 | 24.144 | 24.306 | 24.265 | 1 | Phenol, 2,4-dimethyl- | H | 0.041 |
| 6 | 24.386 | 8969934 | 24.306 | 24.432 | 24.385 | 1 | Phenol, 2,3-dimethyl- | H | 0.058 |
| 7 | 25.503 | 14615040 | 25.456 | 25.648 | 25.564 | 1 | Phenol, 2-methoxy-3-methyl- | G | 0.094 |
| 8 | 26.26 | 41149878 | 26.05 | 26.405 | 26.222 | 1.42 | Creosol | G | 0.377 |
| 9 | 26.74 | 8650653 | 26.675 | 26.79 | 26.748 | 1.17 | 1,2-Benzenediol | G ' | 0.065 |
| 10 | 26.934 | 12062064 | 26.87 | 27.042 | 26.983 | 1 | Phenol, 2,4,6-trimethyl- | H | 0.078 |
| 11 | 28.533 | 9135483 | 28.469 | 28.579 | 28.488 | 1 | Phenol, 2-ethyl-6-methyl- | H | 0.059 |
| 12 | 29.668 | 6107376 | 29.623 | 29.719 | 29.627 | 1 | 1,2-Benzenediol, 3-methyl- | G ' | 0.039 |
| 13 | 31.928 | 71225542 | 31.61 | 32.097 | 31.858 | 1.65 | 2-Methoxy-4-vinylphenol | G | 0.759 |
| 14 | 33.377 | 6796485 | 33.24 | 33.438 | 33.363 | 1 | Phenol, 4-(2-propenyl)- | H | 0.044 |
| 15 | 33.639 | 25258730 | 33.438 | 33.735 | 33.54 | 0.89 | Phenol, 2,6-dimethoxy- | S | 0.145 |
| 16 | 35.859 | 9018212 | 35.741 | 35.935 | 35.772 | 0.92 | Vanillin | G | 0.054 |
| 17 | 37.543 | 13722726 | 37.391 | 37.623 | 37.54 | 1.24 | 3,5-Dimethoxy-4-hydroxytoluene | S | 0.11 |
| 18 | 37.718 | 25808491 | 37.623 | 37.865 | 37.746 | 1 | Phenol, 2-methoxy-4-(1-propenyl)-, (Z)- | G | 0.167 |
| 19 | 39.276 | 5145267 | 39.21 | 39.348 | 39.302 | 1 | Apocynin | G | 0.033 |
| 20 | 40.575 | 8240295 | 40.418 | 40.723 | 40.418 | 1 | Phenol, 2-methoxy-4-(2-propenyl)-, acetate | G ' | 0.053 |
| 21 | 43.06 | 8055674 | 42.993 | 43.12 | 43.062 | 1 | 1-Propiovanillone | G | 0.052 |
| 22 | 45.383 | 19720940 | 45.323 | 45.413 | 45.413 | 2.51 | (Z)-4-Propenylsyringol | S | 0.32 |
| 23 | 45.48 | 26446640 | 45.413 | 45.518 | 45.511 | 1 | Benzenepropanol, 4-hydroxy-3-methoxy- | G | 0.171 |
| 24 | 48.5 | 7572086 | 48.353 | 48.566 | 48.469 | 1 | Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- | S | 0.049 |
| 25 | 59.418 | 201388819 | 59.039 | 59.476 | 59.409 | 1 | Fluoranthene | I.S. | |

**Appendix Table 11.** ***Acer Palmatum Var.*** **Py-GC/MS Results**

| No. | Signal: PYGC-11.D\FID1A.ch | | | | Library | | | | Concentration(mg/g) |
|---|---|---|---|---|---|---|---|---|---|
| | RT*sample* | Area | Start Time | End Time | RT*library* | Rf Value | Name | Type | |
| 1 | 15.718 | 7472595 | 15.638 | 15.938 | 15.854 | 0.59 | Phenol | H | 0.241 |
| 2 | 19.416 | 18541874 | 19.202 | 19.633 | 19.539 | 0.59 | Phenol, 2-methyl- | H | 0.599 |
| 3 | 19.771 | 20122530 | 19.633 | 20.022 | 19.71 | 1 | Benzene, propoxy- | H ' | 1.102 |
| 4 | 21.219 | 65345722 | 21.066 | 21.335 | 21.147 | 1.42 | Phenol, 2-methoxy- | G | 5.08 |
| 5 | 22.323 | 4339964 | 22.206 | 22.398 | 22.222 | 1 | Phenol, 2,6-dimethyl- | H | 0.238 |
| 6 | 24.225 | 4094082 | 24.193 | 24.281 | 24.265 | 1 | Phenol, 2,4-dimethyl- | H | 0.224 |
| 7 | 24.353 | 8146166 | 24.281 | 24.395 | 24.385 | 1 | Phenol, 2,3-dimethyl- | H | 0.446 |
| 8 | 25.301 | 25720803 | 25.149 | 25.433 | 25.186 | 1 | Phenol, 4-ethyl | H | 1.408 |
| 9 | 25.472 | 15608298 | 25.433 | 25.633 | 25.564 | 1 | Phenol, 2-methoxy-3-methyl- | G | 0.854 |
| 10 | 26.255 | 60702118 | 26.025 | 26.4 | 26.222 | 1.42 | Creosol | G | 4.719 |
| 11 | 26.737 | 21625122 | 26.565 | 26.873 | 26.748 | 1.17 | 1,2-Benzenediol | G ' | 1.385 |
| 12 | 27.708 | 4577110 | 27.64 | 27.821 | 27.738 | 1 | 4-Vinylphenol | H | 0.251 |
| 13 | 28.538 | 27184467 | 28.399 | 28.787 | 28.488 | 1 | Phenol, 2-ethyl-6-methyl- | H | 1.488 |
| 14 | 29.797 | 5897448 | 29.734 | 29.86 | 29.821 | 1 | 3,5-Dimethoxytoluene | G ' | 0.323 |
| 15 | 31.91 | 63255848 | 31.571 | 32.08 | 31.858 | 1.65 | 2-Methoxy-4-vinylphenol | G | 5.714 |
| 16 | 33.374 | 5950614 | 33.234 | 33.433 | 33.363 | 1 | Phenol, 4-(2-propenyl)- | H | 0.326 |
| 17 | 33.609 | 25554825 | 33.433 | 33.725 | 33.54 | 0.89 | Phenol, 2,6-dimethoxy- | S | 1.245 |
| 18 | 35.813 | 8036379 | 35.7 | 36.06 | 35.869 | 1 | Phenol, 2-methoxy-4-(1-propenyl)- | G | 0.44 |
| 19 | 37.477 | 9119852 | 37.345 | 37.567 | 37.54 | 1.24 | 3,5-Dimethoxy-4-hydroxytoluene | S | 0.619 |
| 20 | 37.699 | 33882855 | 37.567 | 37.837 | 37.746 | 1 | Phenol, 2-methoxy-4-(1-propenyl)-, (Z)- | G | 1.855 |
| 21 | 39.263 | 4384385 | 39.195 | 39.4 | 39.302 | 1 | Apocynin | G | 0.24 |
| 22 | 47.242 | 4689233 | 47.174 | 47.391 | 47.388 | 2.51 | (E)-4-Propenylsyringol | S | 0.644 |
| 23 | 48.472 | 3407228 | 48.393 | 48.607 | 48.469 | 1 | Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- | S | 0.187 |
| 24 | 59.278 | 23745936 | 59.053 | 59.527 | 59.409 | 1 | Fluoranthene | I.S. | |

## Appendix Table 12. Lignin-derived Compound Structures by Py-GC/MS

| Compound Name | Type | Structure | Compound Nam | Type | Structure |
|---|---|---|---|---|---|
| Phenol, 2-methoxy- | G |  | Vanillin | G |  |
| Phenol, 2-methoxy-3-methyl- | G |  | 3,5-Dimethoxy-4-hydroxytoluene | S |  |
| Creosol | G |  | Butylated Hydroxytoluene | H ' |  |
| Apocynin | G |  | Phenol, 2-methoxy-4-(2-propenyl)-, acetate | G ' |  |
| 1,2-Benzenediol, 3-methoxy- | S ' |  | Phenol, 2-methoxy-4-(1-propenyl)-, acetate | G ' |  |
| t-Butylhydroquinone | G ' |  | Benzenepropanol, 4-hydroxy-3-methoxy- | G |  |
| Phenol, 4-ethyl | H |  | (E)-4-Propenylsyringol | S |  |
| Phenol, 2,4,6-trimethyl- | H |  | 4-Acetoxy-3,5-dimethoxybenzaldehyde | S ' |  |

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